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Federal Water Quality Administration
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# REMOVAL OF ORGANICS FROM WASTEWATER BY ACTIVATED CARBON

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A 0.3-million gal./day, four-stage, fixed-bed, granular activated carbon pilot plant, complete with thermal regeneration facilities, continuously treated unfiltered, activated sludge wastewater treatment plant effluent for a four-year period. High-quality product water characterized by a COD of 10 mg./liter was produced on a routine basis. A 17% decrease in carbon capacity occurred between the first and fourth cycles (one cycle per year), at which time a steady state condition was established at a capacity between 45 to 50 lb. of dissolved COD per 100 lb. of carbon. Regeneration of the carbon was shown to be a feasible process and successful backwashing of the first stage carbon, which serves as a filter and an adsorber, made pretreatment of the wastewater treatment plant effluent unnecessary. The estimated cost of $86 per million gallons, for a 10-million gal./day carbon plant is based on a fourth cycle dosage of 350 lb. of carbon per million gallons of water and a conservative carbon loss of 10% per cycle.

The Federal Water Quality Administration and the Los Angeles County Sanitation Districts, through a contractual agreement, operate an advanced waste treatment research facility on the grounds of the Pomona Water Renovation Plant in Pomona, California. The overall objective at Pomona is the development of the minimum cost technology capable of renovating wastewater. In order to attain this objective, the most promising available treatment processes are being field tested and evaluated on a pilot-plant scale.

The removal of residual dissolved and suspended organic matter from municipal wastewater treatment plant effluents is a necessary step if this water is to be reused. It has been demonstrated at Pomona that the use of a granular activated carbon column is a feasible process for accomplishing this removal.

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Since June of 1965, a 0.3-million gal./day, four-stage, fixed-bed, granular activated carbon pilot plant, complete with thermal regeneration facilities, has been continuously treating unfiltered activated sludge plant effluent from the Pomona Water Renovation Plant. The objective is to obtain reliable cost and operating data on the use of granular carbon and to establish its effectiveness, after repeated adsorption cycles, in removing dissolved and suspended organic matter that vary in type and concentration due to the conditions of daily and seasonal flow fluctuations that occur in municipal waste streams.

## PILOT-PLANT DESCRIPTION

The pilot plant components include five carbon vessels or contactors, influent and product water storage tanks, a carbon dewatering bin, a quench tank, and a regeneration furnace, all mounted on a concrete slab with related piping, pumps, and controls. The slab is 44 ft. sq. and sloped to drain into the quench tank pit in order to facilitate the recovery of any accidentally spilled carbon. A photograph of the carbon pilot plant is presented in Figure 1.

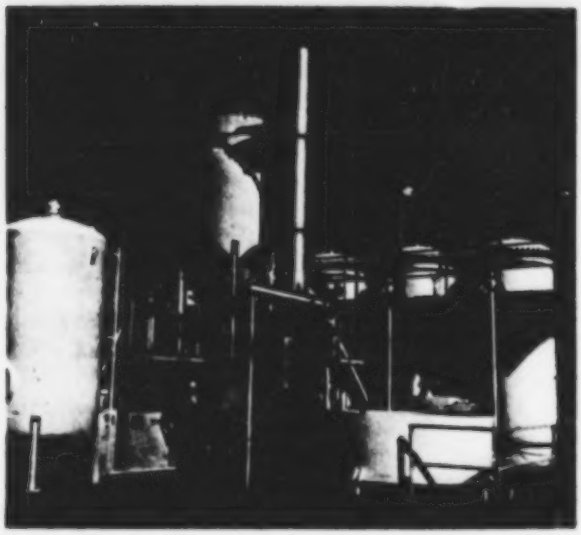

Fig. 1. Granular activated carbon pilot plant.

A schematic flow diagram for the pilot plant is shown in Figure 2. Initially, chlorinated secondary effluent was used since it was more conveniently available from the water renovation plant. However, during the course of the study the plant was enlarged by the construction of a new parallel treatment plant, and both chlorinated and unchlorinated secondary effluents from either the old or new treatment plants have been used without any significant differences in operation of the carbon columns.

The secondary effluent is directed to the storage tank from where it is pumped into the carbon columns. The pilot plant is composed of two columns, a single-stage and a four-stage; each of the stages or contactors is identical in design and contains 6,700 lb. of 16 × 40 mesh granular carbon having characteristics as shown in Table 1. The contactors are 6 ft. in diameter, have an overall height of 16 ft., and are designed for a working pressure of 50 lb./sq. in. The detailed design is shown in Figure 3. The carbon bed is supported on a Neva-Clog screen system consisting of the Neva-Clog screen, an expanded metal backing, and a series of concentric annular rings which are an integral part of the contactors for structural support. The screen comprises two layers of stainless steel perforated with 1/32-in. diam. holes and spot-welded together with holes off-set from each other.

TABLE 1. CARBON CHARACTERISTICS

| | |
|---|---|
| IODINE NUMBER | 1100 |
| METHYLENE BLUE NUMBER | 300 |
| MOLASSES NUMBER | 220 |
| APPARENT DENSITY | 0.47 g/ml |
| ASH CONTENT | 5% |
| MEAN PARTICLE DIAMETER | 0.90 mm |
| MESH SIZE | 16 x 40 |

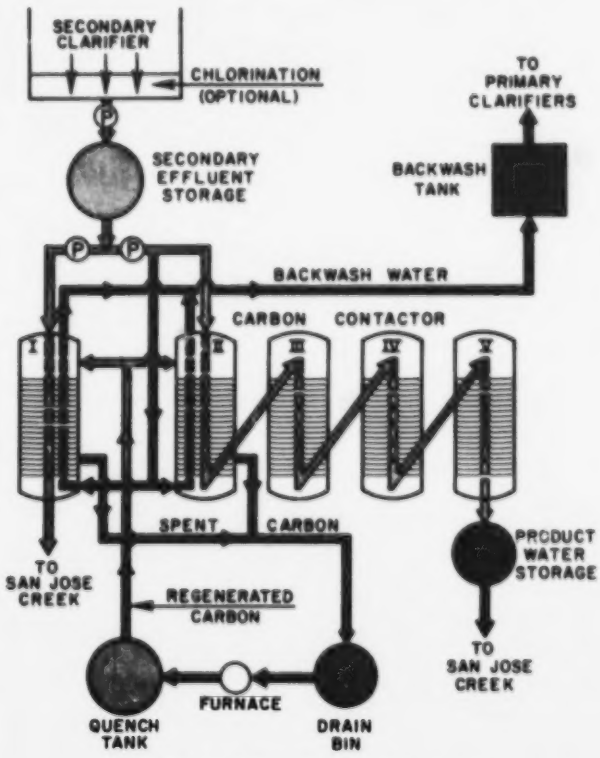


Fig. 2. Schematic flow diagram.

The interiors of the contactors are coated with a coal-tar epoxy compound designed to withstand the corrosive action of the carbon-water environment. One-inch couplings are welded in the contactor walls for sampler connections and pressure taps.

The liquid enters at the top from an annular ring through 20 1-in. holes around the circumference of each contactor. This ring is also used to remove liquid during backwashing. A distance of 3½ ft. between the entrance ring and the top of the carbon bed provides room for a 35 to 40% bed expansion during backwashing.

The single-stage column was designed to provide supplementary data to those obtained from the main four-stage column pilot plant, and is operated at 200 gal./min., or a hydraulic loading of 7 gal./(min.)(sq. ft.), which results in an empty bed detention time of 10 min. The water leaves the column and is discharged to the nearby San Jose Creek.

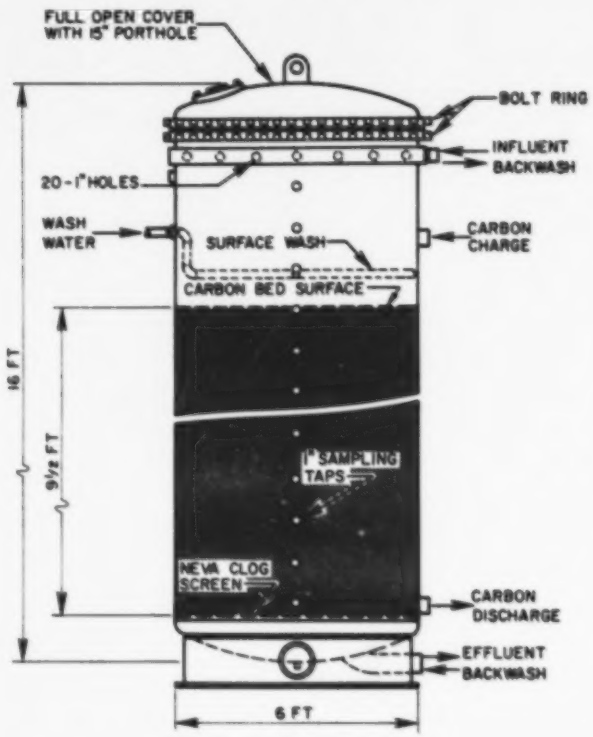


Fig. 3. Typical contactor.

The four-stage column also operates at 200 gal./min. and has an empty bed detention time of 40 min. with the secondary effluent passing, in series, through each of the stages and then to the product water storage tank with overflow entering the creek. As the carbon becomes exhausted, the level of organic matter in the effluent increases and, when it reaches a COD of 12 mg./liter, the first stage is removed from service and the carbon is transferred as a slurry into the dewatering bin. The carbon, with a 40% moisture content, is conveyed into the multiple hearth furnace where it is regenerated at 1,650° to 1,700°F.

The furnace is a 30-in. I.D., vertical, refractory-lined, six-hearth unit, complete with air pollution control equipment. It is natural gas fired and steam is added to enhance the regeneration. Carbon leaves the furnace at 90 lb./hr. and is discharged, under water, into the quench tank from where it is educted into the contactor. Regeneration of one stage requires about 75 hr. to complete.

Carbon losses during regeneration, which average 8½%, are made up with virgin carbon and the contactor is returned to service as the fourth stage of the column. Through valving, the other stages are moved forward one position, thus approaching a countercurrent flow of carbon and water.

Repeated exhaustions and regenerations of the carbon are defined as adsorption cycles. In the four-stage column an adsorption cycle for the column is completed when all of the stages have been exhausted and regenerated once, that is, each contactor has seen service in each stage position. Experience has indicated that regeneration of the first stage is required every 75 days—equivalent to treating about 20 mg. of secondary effluent. On this basis, exhaustion of each of the four stages requires almost one year. At this rate four cycles have been obtained during the period of this study.

In the single-stage column four adsorption cycles are completed in a year's time. This has allowed evaluation of the effect of nine cycles on carbon efficiency and eleven cycles on carbon attrition and regeneration characteristics. During the last two cycles special studies were conducted with secondary effluent which did not include the monitoring of dissolved COD removal, but did require carbon regeneration. Although its operation is different from that of the main four-stage pilot plant, the single-stage column has provided valuable additional supporting data.

## PILOT-PLANT PERFORMANCE

### OPERATION

Backwashing of both the single-stage column and the first stage of the four-stage column is performed on a daily basis to free the carbon bed of trapped suspended solids removed by filtration from the secondary effluent. Backwashing is accomplished using secondary effluent at hydraulic loading rates up to 7 gal./(min.)(sq. ft.) and a volume of water equivalent to 3 to 4% of the daily column flow.

Pressure loss data in the carbon for each stage of the four-stage column, before and after backwashing the first stage, are shown in Table 2. After backwashing the first stage, the column has a total pressure drop of about 21 lb./sq. in. which increases to 32 lb./sq. in. over an average 24-hr. period. This increase, as presented in Table 2, is due to filtration of suspended solids by the first stage carbon resulting in a 10 lb./sq. in. pressure loss increase in this stage.

The second stage must also be backwashed to maintain the column operating pressures within the capacity

TABLE 2. EFFECT OF STAGE A BACKWASH ON PRESSURE LOSS

| | PRESSURE LOSS (PSI) | | | | |
|---|---|---|---|---|---|
| | STAGE A | STAGE B | STAGE C | STAGE D | TOTAL |
| BEFORE BACKWASH | 16.8 | 5.2 | 4.0 | 5.6 | 31.6 |
| AFTER BACKWASH | 6.6 | 4.9 | 4.0 | 5.2 | 20.7 |

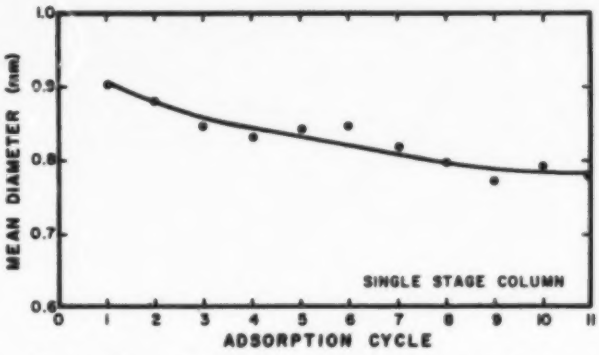


Fig. 4. Effect of adsorption cycle on carbon particle size.

of the pumping system. This is required, on the average, once or twice per month.

The use of granular activated carbon in a column system requires that it be regenerated, transported to and from the regeneration facilities, and routinely backwashed. As a result of those operations, attrition of the carbon particles occurs. Data showing the effects of carbon regeneration and handling on the mean particle diameter are presented in Figure 4. A 13% decrease in the particle diameter of the carbon in the single-stage column occurred after seven adsorption cycles, at which time no further significant changes in the size took place. This is primarily caused by the addition to the column of virgin makeup carbon, which has a mean particle diameter of 0.9 mm., after each regeneration to replace losses. Also, as the supply of the original 16 × 40 mesh carbon was depleted, Filtrasorb 400 (12 × 40 mesh carbon having a mean particle diameter of about 1 mm.) was purchased and used as makeup after the seventh cycle.

In addition to the reduction in the carbon particle size previously described, which has not caused any significant difference in the carbon column operation or pressure drop, a loss of carbon occurs during the regeneration process. This loss has ranged from 11% during the first cycle to 7% during the fourth, and has averaged 8½% during the four-year study.

## ADSORPTIVE CAPACITY

The COD test has been used as the primary parameter for determining the efficiency of the carbon columns in removing both suspended and dissolved organic matter. Since carbon serves as a filtration medium as well as an adsorbant, the COD of the secondary effluent and carbon effluent was determined on both unfiltered and filtered (0.45 $\mu$, membrane filter) samples and values for total COD and dissolved COD (filtered) are reported.

The data in Figure 5 show the distribution of COD removal in the four-stage column. The dissolved COD data indicate about equivalent removal in each of the stages. However, the total COD data show that 46% is removed

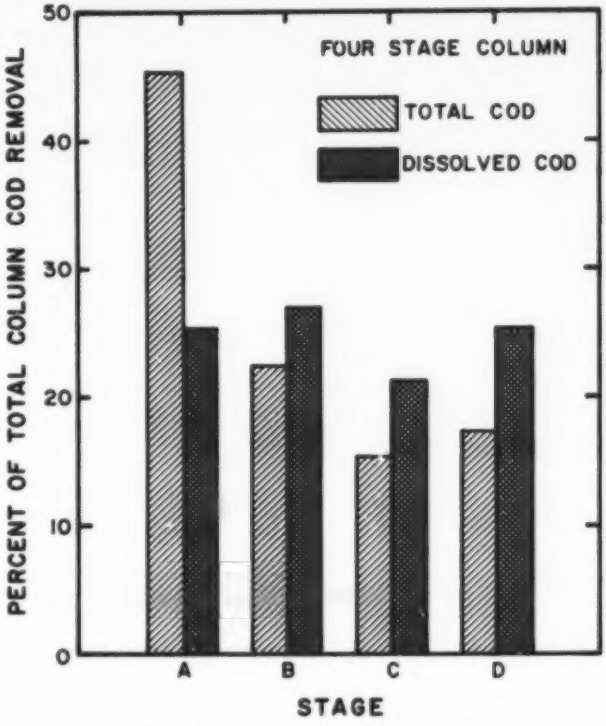


Fig. 5. Distribution of COD removal.

in the first stage. This difference is due to filtration of suspended COD which accounts, on the average, for 20 to 30% of the total COD. Therefore, when monitoring the effect of repeated adsorption cycles on the carbon efficiency, it is necessary that a measurement of the dissolved organic matter be made. A carbon column even after its adsorptive capacity is exhausted will continue to remove suspended COD.

The effect of adsorption cycle on the dissolved COD removal performance of the four-stage column is shown by the data in Figure 6. Each of the data points represents a regeneration of the first-stage column; four such regenerations are equivalent to an adsorption cycle. The

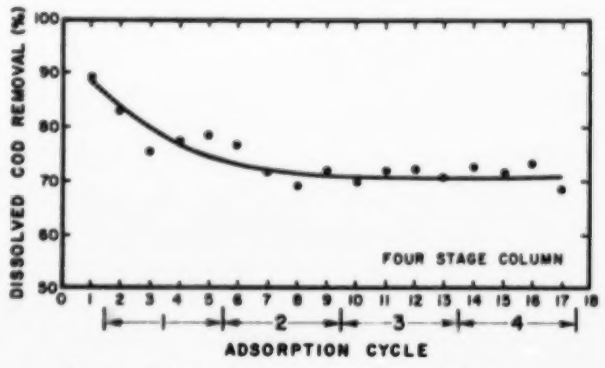


Fig. 6. Effect of adsorption cycle on COD removal.

data clearly indicate that a reduction in COD removal occurs from an initial level of 89 to 71% after one and one-half adsorption cycles, and that the removal remains constant through the remaining cycles.

Comparable data for the single-stage column are presented in Figure 7. The dissolved COD removal decreased from an initial value of 53 to 40% during the sixth cycle, after which time the removal stabilized at the 40% level. The addition of 8½% virgin makeup to replace losses during each cycle has had the effect of upgrading the adsorption capacity of the carbon. If this loss rate is decreased, the loss in capacity with adsorption cycle will be greater.

The effect of repeated adsorption cycles on the adsorptive capacity of carbon can be expressed in terms of its capacity for a given adsorbate under specific laboratory conditions. One of the adsorbates used to characterize the adsorptive properties of activated carbon is iodine. The standard iodine number test is used to measure the extent of recovery of the adsorptive capacity or the extent to which the micropores (less than 20 Å.) have been cleared of adsorbed organics by regeneration. Data in Figure 8 show the iodine number for both spent (exhausted) and regenerated carbons from the single- and four-stage columns after repeated cycles.

The initial iodine number of the virgin carbon was 1,100 and after eleven adsorption cycles in the single-stage column the iodine number was reduced to 608, which is a 45% decrease, with every indication that further reductions will take place. An even greater decrease with adsorption cycle is noted in the iodine number of the regenerated carbon in the four-stage column. This continuous decrease in the adsorptive capacity of the carbon for iodine indicates that the micropores have not been cleared of adsorbates during regeneration. However, previous data shown in Figures 6 and 7 relate COD removal to adsorption cycle and indicate a 20% reduction in efficiency in the four-stage column during the first two cycles, after which time the removal remains constant. Iodine is therefore not typical of the organic matter in secondary effluent, and although the surface area in the micropores has continued to decrease, the capacity of the carbon for organic matter as measured by dissolved COD has not followed suit.

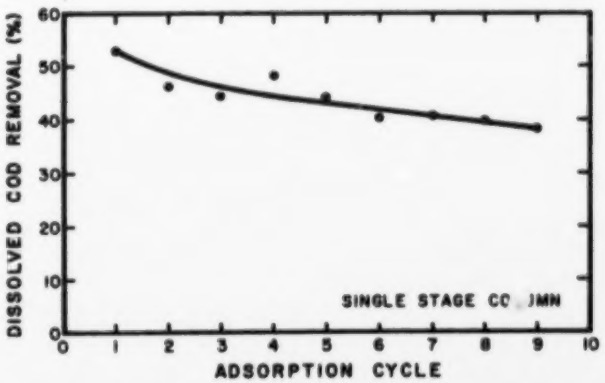


Fig. 7. Effect of adsorption cycle on COD removal.

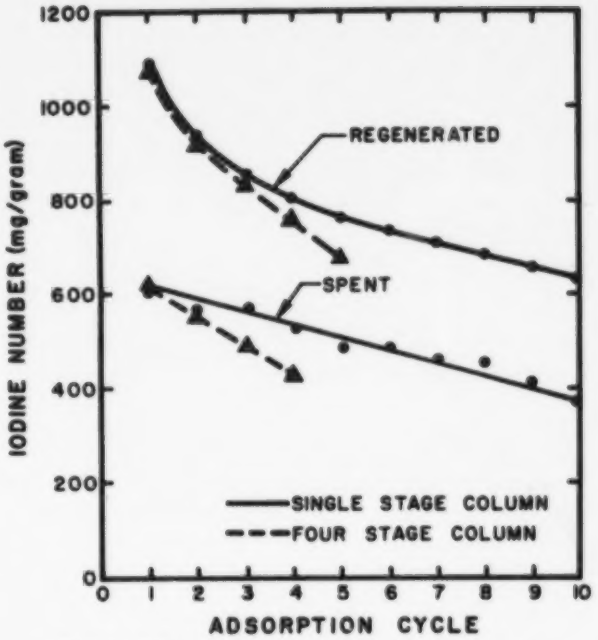


Fig. 8. Effect of adsorption cycle on iodine number.

The iodine number of spent carbon as shown in Figure 8 also shows a steady decrease for both single-stage and four-stage columns. The difference between the regenerated and spent iodine numbers, or iodine capacity used, is due to the presence of substances in the micropores that were removed from the water during operation of the column. The data indicate that the amount of capacity used reaches a steady state condition after the third cycle.

Since carbon capacity can have a significant effect on the economical feasibility of carbon adsorption as a process for removing organic matter from secondary effluent, it is necessary to ascertain the effect of repeated adsorption cycles on the virgin or original capacity. Data showing this effect are presented in Figure 9. The total COD capacity is somewhat variable and is primarily due to the variability of the suspended solids in the secondary effluent which accounts for 20 to 30% of the total COD. The dissolved COD in the secondary effluent, which is significantly less variable, shows a more consistent relationship between capacity and adsorption cycle. It has been previously mentioned that dissolved COD was chosen as the primary parameter to measure the change in adsorptive capacity. The capacity is expressed in pounds of COD adsorbed per 100 pounds of carbon and has decreased 17% after four adsorption cycles. The

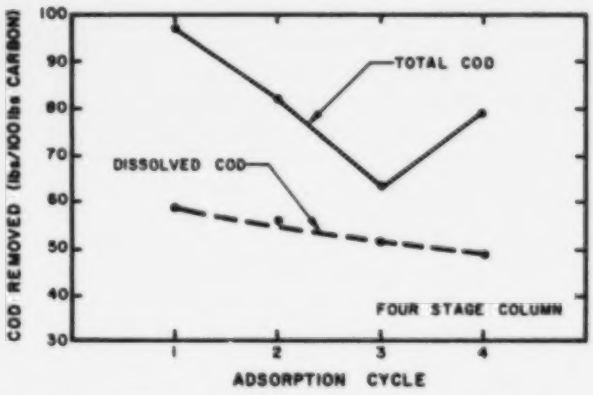


Fig. 9. Effect of adsorption cycle on carbon capacity.

change in capacity between the third and fourth cycles has decreased less than that of the early cycles, indicating that a steady state condition is being reached at 45 to 50 lb./100 lb.

It has been established through operating experience at Pomona that biological oxidation of organic matter takes place in carbon. The single-stage column during a special long-term study was never completely exhausted and continued to remove 2 to 4 mg./liter of dissolved COD at the end of a nine-month period; for this reason biological action undoubtedly contributes to increasing the carbon capacity above that occurring from true adsorption phenomena.

The relationship between carbon dosage and adsorption cycle is shown in Figure 10 and indicates that a steady state condition was reached after the third cycle at 350 lb. of carbon per million gallons.

## WATER QUALITY

The average quality characteristics of the four-stage column influent and effluent from June, 1965, to July, 1969, are shown in Table 3. The total COD of the effluent has averaged 10 mg./liter during this period with

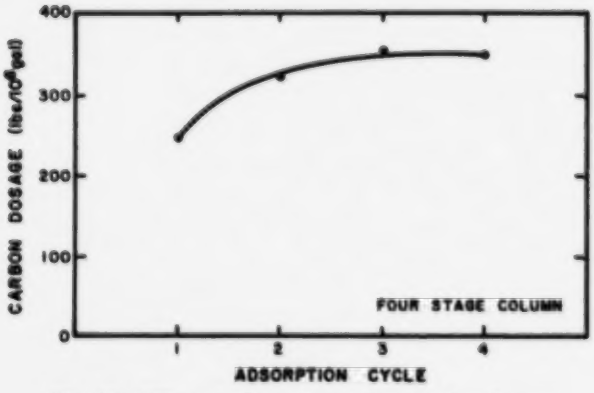


Fig. 10. Effect of adsorption cycle on carbon dosage.

TABLE 3. CARBON ADSORPTION PILOT PLANT; AVERAGE WATER QUALITY CHARACTERISTICS (JUNE 1965 TO JULY 1969)

| PARAMETER | | INFLUENT | EFFLUENT |
|---|---|---|---|
| SUSPENDED SOLIDS | mg/l | 9 | 0.0 |
| COD | mg/l | 43 | 10 |
| DISSOLVED COD | mg/l | 30 | 8 |
| TOC | mg/l | 12 | 3 |
| NITRATE as N | mg/l | 8.1 | 6.6 |
| TURBIDITY (Jtu) | | 8.2 | 1.2 |
| COLOR (Platinum-Cobalt) | | 28 | 3 |
| ODOR | | 12 | 1 |
| CCE | mg/l | - | 0.026 |
| BOD | mg/l | 3 | 1 |

yearly averages ranging from 9.3 to 10.5 mg./liter. In order to evaluate the performance of the column after repeated adsorption cycles, it was necessary to maintain a constant effluent quality in order to eliminate this as a variable in determining carbon dosage and capacity.

The U. S. Public Health Service Drinking Water Standards for 1962 limit the concentration of carbon chloroform extract (CCE) in a water supply to 0.2 mg./liter. The CCE present in the carbon effluent has averaged 0.026 mg./liter, which is an order of magnitude less than that required for potable water.

The removal of turbidity and suspended solids is due to filtration by the carbon and takes place primarily in the first stage.

A limited quantity of nitrate is removed in the column and, at an influent concentration of 8.1 mg./liter ($NO_3$—N), amounts to a 19% reduction and is due to biological denitrification in the carbon.

## COST ESTIMATE

A cost estimate for a 10-million gal./day, four-stage carbon plant based on the operating results obtained during the four-year pilot-plant study is detailed in Table 4. The capital equipment cost of $\$1.86 \times 10^6$ was amortized over 20 years at 5% interest and amounts to 48% of the total cost of $86 per million gallons for carbon treatment. This estimate is based on a plant that would provide product water having the quality characteristics shown in Table 3. Cost and quality are interrelated variables and must be considered together. For example, if a product water with an average total COD of 15 mg./liter was desired it could be provided at a cost less than $86 per million gallons.

The cost of makeup carbon was determined using a dosage of 350 lb. of carbon per million gallons of water as shown in Figure 10. A conservative loss of 10% was also applied to estimate a makeup carbon cost of $11 per million gallons.

TABLE 4. CARBON ADSORPTION PROCESS; COST ESTIMATE—10 MILLION GAL./DAY PLANT

| AMORTIZATION OF CAPITAL | | $/10^6 GALLONS |
|---|---|---|
| $1,860,000; 20 years @ 5% | | 41.00 |
| OPERATION AND MAINTENANCE | | |
| POWER | $ 8.50 | |
| LABOR | 18.00 | |
| MAINTENANCE MATERIALS | 5.00 | |
| CARBON REGENERATION | | |
| POWER, GAS AND WATER | 2.50 | |
| MAKEUP CARBON (10% Loss) | 11.00 | |
| | | 45.00 |
| TOTAL | | $86.00 |


## SUMMARY

A 0.3-million gal./day, four-stage, fixed-bed, granular activated carbon pilot plant has continuously treated unfiltered activated sludge plant effluent from the Pomona Water Renovation Plant from June, 1965, through July, 1969. Extensive operating data collected during four adsorption cycles, which required four years to complete, indicated that a high-quality product water, characterized by an average dissolved COD of 8 mg./liter was produced on a routine basis. This water contained, on the average, a concentration of carbon chloroform extract (CCE) equivalent to 0.026 mg./liter, which is significantly less than that required by U.S. Public Health Service standards for potable water.

Successful backwashing of the first-stage carbon, which serves as a filter and an adsorber, made pretreatment of the secondary effluent unnecessary. The filtering action of the carbon readily removed the 9 mg./liter of suspended solids present in the activated sludge plant effluent. This filtration causes, on the average, a 10 lb./sq. in. increase in the pressure loss over a 24-hr. service period. Partially due to filtration, 46% of the total COD that is removed by the four-stage column is removed in the first stage. About equal removals of dissolved organic matter, represented by dissolved COD, occur in each stage.

Removal efficiency of dissolved COD was greater than anticipated, amounting to a carbon capacity of 59 lb./100 lb. of carbon during the first cycle. A 17% decrease in the carbon capacity occurred between the first and fourth cycles, which resulted in a fourth cycle capacity of 49 lb. of dissolved COD per 100 lb. of carbon. The data indicate that a steady state condition is being reached at a capacity of 45 to 50 lb./100 lb. of carbon.

Routine column performance data show that 89% of the secondary effluent dissolved COD was removed during the first cycle, which decreased to 71% during the second cycle after which the removal approached a steady state condition. Following an increase in the carbon dosage from 250 lb. of carbon per million gallons during the first cycle, the dosage remained constant during both the third and fourth cycles at 350 lb. per million gallons.

Regeneration of the carbon was shown to be a feasible process and has been routinely accomplished. Iodine number determinations confirm that a decrease in adsorptive capacity takes place and that the micropores (less than 20 Å.) in the carbon cannot be completely cleared of adsorbed organics by thermal regeneration. However, the iodine molecule is not characteristic of typical organic matter in secondary effluent and consequently, as the data show, is not a satisfactory parameter for determining the effect of repeated adsorption cycles on the capacity of carbon for dissolved COD.

Data collected from a separate, parallel, single-stage column designed to provide supplementary information to that collected from the four-stage column indicated a 13% decrease in the mean particle diameter of the carbon after seven adsorption cycles, at which time a steady state condition existed. No significant differences in column operation or in pressure loss in the carbon resulted due to the decrease in particle size from 0.90 to 0.79 mm.

An estimate for a 10-million gal./day, four-stage carbon pilot plant designed to produce a product water with a dissolved COD of 8 mg./liter was made. The estimated cost of $86 per million gallons is based on a fourth cycle carbon dosage of 350 lb. per million gallons of water and a conservative carbon loss of 10% per cycle.


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